Supporting Information of "Comment on 'Toward Unraveling the Puzzle of Sum Frequency Generation Spectra at Interface of Aqueous Methanol Solution: Effects of Concentration-Dependent Hyperpolarizability' "

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In this Supporting Information, we describe the details of MD analysis of $\rho \langle \cos \theta \rangle$.

S1 MD Conditions

Here we describe the outline of the present computation. We employed the SPC model for water,¹ and OPLS-AA force fields for methanol,² which are the same as the force fields employed in Ref.³ We prepared the methanol/water mixtures with varying concentration from pure water (mole fraction x = 0) to pure methanol (x = 1) with a 0.1 interval of the mole fraction x. These molecules at each concentration x are enclosed in a periodic rectangular unit cell of $L_x \times L_y \times L_z = 30$ Å $\times 30$ Å $\times 200$ Å with three-dimensional periodic boundary conditions. The total numbers of molecules contained in a unit cell were set to 1000 for x < 0.5 and 500 for otherwise.⁴

To prepare the initial configurations of the liquid slab, water and methanol molecules were placed in random positions and orientations by PACKMOL package⁵ to form a liquid slab. Newton's equation of motion was solved with leap frog algorithm with time step $\delta t = 1.0$ fs in three-dimensional periodic boundary conditions. The *NVT* (constant volume and temperature) ensemble simulation was carried out, where the system temperature was kept at T = 300 K with Nosé-Hoover thermostat.^{6,7} The long-range Coulombic interaction was treated with the particle-mesh Ewald method.^{8,9} The cutoff length of the Lennard-Jones and the real-space part of the Ewald sum were taken to be 12 Å. MD simulations of water/methanol mixture were performed during 150 ns for each trajectories with 8 parallel computation starting from different initial configuration. The initial 50 ns trajectories (0 ns < t < 50 ns) were used as the equilibration run, and the subsequent trajectories with 50 ns (50 ns < t < 100 ns) were used as the production run. Gromacs package (version 5.1.2)¹⁰ was employed for the trajectory calculation.

S2 Results and discussion

Figure S1 shows the density profile of methanol $\rho(\text{met})$ in methanol/water mixtures in Panel (a), orientational profile of methanol $\langle \cos \theta \rangle$ in Panel (b), and these product $\rho(\text{met}) \langle \cos \theta \rangle$ in Panel (c) as a function of depth coordinate \hat{Z} . θ is defined as an angle between surface normal from liquid to vapor and the vector of the methyl C_{3v} axis. Similar to the case of the previous polarizable MD simulation,⁴ $\rho(\text{met})$ in the present non-polarizable simulation also shows a surface enhancement at a low concentration of methanol due to the existence of the hydrophobic methyl group, and a ordinary density profile of pure liquid at a high concentration. $\langle \cos \theta \rangle$ distribution in Fig. S1 (b) shows positive sign near the interface, indicating that the methyl directs their protons toward the vapor phase, and the distributions are gradually suppressed with increasing the concentration of methanol x. This indicates that the orientation becomes randomized with increasing methanol concentration at the interfacial region due to loss of H-bond acceptor.⁴ The product of $\rho(\text{met})$ and $\langle \cos \theta \rangle$ shown in Fig. S1 (c), which corresponds to the response of $\text{Im}[\chi^{(2)}]$ spectra for methyl symmetric stretch mode, manifests that its peak value gradually increases with increasing x for 0.0 < x < 0.5, and decreases for 0.5 < x < 1.0.

To observe the concentration dependence of $\rho(\text{met})\langle\cos\theta\rangle$ profile, the integral values of $\rho(\text{met})\langle\cos\theta\rangle$ distribution in Fig. S1 (c) with respect to \hat{Z} from $\hat{Z} = -15$ Å to $\hat{Z} = 10$ Å as a function of x are plotted in Fig. S2 in black solid line. In Fig. S2, we also plot the values averaged during additional 50 ns MD simulation (100 ns < t < 150 ns) to check the convergence of the statistical data in red dashed line. One can confirm the present results are well converged within the present computational time. Figure S2 clearly shows the turnover behavior of the integral values, which is consistent to the observation in VSFG experiment and is inconsistent to the calculation by Li *et al.*³

The paper reported by Li *et al.* describes, in the caption of Fig. S6 of Ref.,³ that "As suggested by Ishihara *et al.*,⁴ the interfaces in the present work were defined as the regions where both the number density and $\langle \cos \theta \rangle$ of the methanol molecules are nonzero." In our



Figure S1: (a) Density profile of methanol $\rho(\text{met})$ in methanol/water mixtures, (b) orientational profile of methanol $\langle \cos \theta \rangle$, and (c) these product $\rho(\text{met}) \langle \cos \theta \rangle$ as a function of the depth coordinate \hat{Z} , where the origin of \hat{Z} is set to the Gibbs dividing surface of methanol for each density.



Figure S2: The integral of $\rho(\text{met})\langle\cos\theta\rangle$ distribution in Fig. S1 (c) with respect to \hat{Z} from $\hat{Z} = -15$ Å to $\hat{Z} = 10$ Å as a function of x. The solid black line denotes the result averaged during 50 ns < t < 100 ns, and the dashed red lines denotes that averaged during 100 ns < t < 150 ns.

previous study,⁴ the surface density of methanol $\rho^s(\text{met})$ and the surface orientation $\langle \cos \theta \rangle^s$ were evaluated by introducing the following formula.

$$\rho^{s}(\text{met}) = \frac{\int w(Z)\rho(\text{met})(Z)dZ}{\int w(Z)dZ}$$
(S1a)

$$\langle \cos \theta \rangle^s = \frac{\int w(Z) \langle \cos \theta \rangle dZ}{\int w(Z) dZ}$$
 (S1b)

$$w(Z) = \rho(\text{met}) \langle \cos \theta \rangle$$
 (S1c)

where w(Z) is the weighting factor to evaluate the surface values, and we employed $\rho(\text{met})\langle\cos\theta\rangle$ for w(Z) because $\rho(\text{met})\langle\cos\theta\rangle$ has the positive value only at the interfacial region, as shown in Fig. S1(c). In Fig. S3, the results of $\rho^s(\text{met})$ in panel(a), $\langle\cos\theta\rangle^s$ in panel(b), and these product $\rho^s(\text{met})\langle\cos\theta\rangle^s$ in panel(c) are shown, and compared the results of the present MD simulation in the left panels with those evaluated by the MD by Li *et al.* (Fig. S7 and Fig. 4b in Ref.³) in the right panels. Although the qualitative behaviors of Panels (a) and (b) in Fig. S3, which shows monotonic increase of $\rho^s(\text{met})$ and monotonic decrease of $\langle \cos \theta \rangle^s$, are consistent with each other, the results of panel(c) are inconsistent. The present result, Fig. S3 (c1), clearly shows the turnover behavior for $\rho^s(\text{met})\langle\cos\theta\rangle^s$, which is consistent to the result in Fig. S2, whereas the result by Li *et al.* shows a monotonic increase. The reason of this discrepancy is not clear at present, but the present MD simulation with the non-polarizable model demonstrates that the turnover behavior of $\chi^{(2)}$ observed for the methyl symmetric stretching mode in VSFG experiment can be explained by the orientational effect.



Figure S3: (a) Surface density of methanol ρ^s (met), (b) surface orientation $\langle \cos \theta \rangle^s$, and (c) these product ρ^s (met) $\langle \cos \theta \rangle^s$. The left panels are the results of the present MD simulation, and the right panels are the results (Fig. S7 and Fig. 4b in Ref.³) by Li *et al.* (Reprinted with permission. Copyright 2019 American Chemical Society.) This is the same figure with Fig. 2 of the main text.

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